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CO_2-Enhanced Transport of Small Molecules in Thin Films: A Fluorescence Study

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ABSTRACT: Steady-state fluorescence measurements have been used to measure the rate of transport of a fluorescent probe (pyrene) out of ca. 250 nm thick films of polystyrene in contact with CO_2(sc) at pressures in the range 35−110 bar (estimated CO_2 content in the film up to 0.11 weight fraction) and several temperatures (35, 40, 50, and 60 °C). At constant temperature, the estimated pyrene diffusion coefficient increases by approximately 4 orders of magnitude from the lowest to the highest CO_2 content (e.g., from ca. 10^{-14} cm^2/s for ca. 0.04 CO_2 weight fraction to ca. 10^{-10} cm^2/s for ca. 0.11 CO_2 weight fraction at 60 °C). We estimate the glass transition pressure at a given temperature ($P_g(T)$) in two ways: (1) from the inflection point of the log D vs $P(CO_2)$ plot, (2) matching log D at a given temperature and $P(CO_2)$ to the value obtained for an unswollen film at T_g (D is measured by the rate of loss of the probe into a vacuum).

Introduction

The use of CO_2 either as a solvent or as a polymer processing aid has been explored actively for the past few years for a variety of reasons including its low price, the ease of manipulation of its properties by pressure and temperature (including its low critical temperature of 31 °C) and benign environmental effect. It has been demonstrated that the glass transition temperature of many polymers can be significantly lowered by exposure to CO_2, like any swelling solvent.[1] Similarly, the rate of transport of small molecules in to and out of polymers has been demonstrated to increase in the presence of CO_2. However quantification of these effects has occurred more recently, starting with the 1992 paper of Berens et al.[2]

The use of fluorescence techniques to study the movement of either small molecules or tagged polymers in polymer solids has been well established by the groups of Winnik[3] and Torkelson,[4] and these techniques have recently been applied by Gupta et al. to the study of small-molecule probe diffusion in CO_2 swollen polystyrene.[5] Fluorescence techniques are very sensitive such that very small amounts of the fluorescent probe are required. These techniques have the disadvantage that a fluorescent probe may disturb the physical system that is being examined and sometimes there are photophysical complications (e.g., adventitious fluorescence quenching, photobleaching, or photoreactions) that defeat a simple interpretation of the data.

The present paper has the aim of characterizing the rate of transport of a fluorescent probe out of a polymer film that is in contact with CO_2 at various temperatures and pressures and as such can be taken to be complementary to the papers of Chapman et al.[6] and Gupta et al.[5] In the Chapman paper, forced Rayleigh scattering (FRS) is used to monitor the rate at which a photochemically produced asymmetric distribution of the two isomers of azobenzene (a “grating”) in a polystyrene film decays away with time, through a combination of thermal relaxation and diffusion. In the Gupta paper, nonradiative energy transfer between a probe species (energy acceptor) and pyrene-labeled polystyrene (energy donor) was used to obtain the diffusion constant of the small probe molecules (the diffusion of the labeled chain can be assumed to be orders of magnitude slower than the probe). The method we use here is simple to carry out, as we simply observe the loss of fluorescence of a small molecular probe (pyrene) by virtue of its transport out of the film into the CO_2 phase in contact with it. Of course for our method to work it is essential that the probe have sufficient CO_2 solubility that transport out of the film is facile.[7] While many typical fluorescent probes have very low solubility in CO_2, this transport process can still be highly efficient because of their very high diffusion constant in CO_2. The sensitivity advantage of fluorescence techniques can be very important in measurements of diffusion processes. Since the time required for molecular transport out of an object scales like l^2/D (D is the diffusion coefficient of the molecule, and l is the dimension of the object), for small diffusion constants it is essential that l be small in order to keep the experimental time manageable. In the present case we use films of ca. 250 nm thickness and present measurements of the probe diffusion constant as low as ca. 10^{-14} cm^2/s. We would have no difficulty measuring transport processes on films substantially thinner than this but it is expected as the film thickness approaches R_g of the polymer that “confinement effects” would be observed[8] and we will leave this for later studies.

Experimental Section

Preparation of Polymer Films. Pyrene was obtained from Eastman Kodak and used after recrystallization two times from ethyl alcohol. The quality of recrystallized pyrene was checked by its UV absorption and fluorescence spectra. HPLC grade toluene (Aldrich) was used for film formation. Previous work in our labs has established that polystyrene obtained from a commercial polystyrene petri dish (Becton Dickinson Labware) is free from fluorescent impurities. This

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material was purified by triple reprecipitation from methylene chloride and 1,4-dioxane using methanol as a precipitant. The last precipitate was dissolved in 1,4-dioxane, and vacuum freeze-drying was used to remove all solvent in the sample. GPC analysis using UV absorption and differential refractive index detection showed that the purified sample does not contain monomer or oligomer and its number-average molecular weight is about 100K with $M_w/M_n = 1.8$. The films were prepared as follows: 11.0 mg of the purified pyrene was dissolved in 5 mL of toluene. Then 432 mg of the purified polystyrene was dissolved in 7 mL of toluene and 2 mL of the pyrene−toluene solution. The solution was heated to 60 °C and mixed briefly on a Vortex-Genie mixer. The solution was maintained at 60 °C overnight and then was passed through a 0.45 μm pore size PTEF filter. The polystyrene−pyrene film was directly spin-coated onto a polished sapphire window used for the high-pressure fluorescence cell (to be described later) at 5000 rpm using a Photo-Resist Spinner model 1-EC101D-R435(Headway Research Inc.). To relieve any strain in the film, the window plus film was annealed in argon at 110 °C for 1 h before carrying out any fluorescence experiments. Using the above protocol reproducible films of thickness ca. 250 nm could be reliably produced. Additionally evaporative loss of the pyrene reduced its content to approximately 0.3 wt %. Independent DSC measurements of T_g for polystyrene containing 1 wt % of pyrene indicated that T_g was depressed by approximately 0.9 °C, so we assume that we can neglect any plasticization effects by the pyrene probe.

Film thickness was measured using an ALPHA-STEP 200 profilometer (Tencor Instruments) (software version V3.7-2) after fluorescence experiments. The thickness was taken as the average over at least six points on the film, with a standard deviation of ±5 nm). The surface quality of the films and adhesion to the substrate was very good both before and after the fluorescence experiment, as judged by naked eye and during the profilometer measurements. It was verified that the film thickness did not change after exposure to CO_2. Of course the film swells during CO_2 exposure, as will be discussed later.

Fluorescence Instrumentation and Fluorescence Cell. The fluorimeter used was a SPEX Fluorolog-τ2 equipped with a 450 W xenon light source, Czerny-Turner double grating excitation and emission monochromators, and Hamamatsu R928 emission signal and reference photomultipliers. A 1 cm wide quartz cuvette filled with 8 mg/mL solution of rhodamine B in 1,2-propanediol transformed 8% of the excitation photons into red photons that are detected by the reference photomultiplier. This allows fluctuations in the excitation light intensity to be accounted for accurately. The high voltages were 950 and 400 V for signal and reference photomultipliers, respectively. To minimize any photobleaching or other photoreaction VINCENT VS25S1T0 shutters were inserted between excitation beam outlet and sample chamber, controlled by a 1976 accessory controller and DM3000F software through a UniBlitz D122 shutter driver. The shutter opened for 0.5−1.0 s at a time interval determined by the time scale of the experiment (time intervals from 30 to 300 s were typically used but for fast release experiments at higher pressure 1−15 s time intervals were used). The fluorescent cell was like that used in previously reported experiments.[9] The cylindrical cell has a total volume of ca. 30 mL and has two sapphire windows at 180° to each other. The front one has the PS−pyrene film for fluorescence measurements, and the back one is useful for visual observation of an experiment in progress. In some experiments, windows at 90° to the excitation beam have been used to check for the presence of pyrene in the CO_2(sc) phase (see later discussion). In the present experiments front face fluorescence geometry was used with the subject film on the window facing the excitation beam and the fluorescence is collected at approximately 30° off the excitation axis. A small magnetic stirrer bar was placed in the bottom of the fluorescence cell (approximately 2 cm below the excitation beam) to ensure rapid removal of the pyrene from the excitation region after it has diffused from the film. We found a modest degree of stirring to be essential if reproducible data was to be obtained. The temperature of cell was controlled by a Micromega CN77000 temperature controller through two heating tapes and two heating cartridges. The CO_2 was preheated in a reservoir with approximately three times the volume of the fluorescence cell in order to minimize the expansive cooling when it was introduced into the sample compartment.

Fluorescence Experiments. All fluorescence signals were collected using front face geometry as the ratio of the signal to the reference signal (*S*/*R* mode). The width of the excitation and emission monochromator slits was 2 mm (equivalent to 3.4 nm bandwidth) for both emission and excitation spectra. The excitation wavelength of emission spectrum was 340 nm. For all time base scans excitation was at 340 nm with 3.4 nm bandwidth and the emission was collected at 396 nm with 6.8 or 13.6 nm bandwidth. We did not observe any shift in the excitation or emission spectrum of pyrene after the introduction of CO_2. This is expected since the local environment is expected to remain nonpolar with or without CO_2. For each experiment, the cell plus film was positioned in the fluorescence chamber to optimize the signal intensity, then the temperature was equilibrated for both the reservoir of CO_2 and the cell. The CO_2 was introduced into the cell over a period of 5−10 s. The expansion of the gas always results in some cooling which was quickly compensated for by the temperature control system. Obviously during the initial exposure of the polymer to the CO_2 there will be dissolution of the CO_2 in the film and film swelling. Although the fluorescence intensity can be measured immediately after the introduction of the CO_2, the first few points are not expected to be typical of the swollen and equilibrated film, and we typically exclude the initial data from the data analysis (see later discussion).

Loss of Pyrene into Vacuum. By way of comparison with the loss of pyrene by diffusion into CO_2 we also studied the loss of pyrene in a polystyrene film heated while in the presence of a vacuum. We found that the application of a modest vacuum (floor pump with an ultimate vacuum of ca. 20 mTorr plus a liquid nitrogen cold trap) resulted in steady loss of pyrene fluorescence that was very similar to diffusion into CO_2. There was a time delay between the time that heating of the sample compartment was initiated and the sapphire window plus film was judged to be equilibrated. From the point of view of the data analysis (see next subsection), so long as a relatively small fraction of pyrene has escaped from the film the choice of the time point to designate as $t = 0$ is not critical to the analysis. The rate of loss of pyrene into the vacuum depends not only on the diffusivity of the pyrene but also on the vapor pressure of the pyrene at a given temperature (the same would be true for the loss to supercritical CO_2). In these experiments, conducted from 90 to 110 °C, the vapor pressure of pyrene is expected to change by a factor of ca. 5.95,[10] much less than the change of the diffusion constant, so we ignore the effect of the pyrene vapor pressure in the analysis. Furthermore, the relatively change in vapor pressure is not expected to change the value of the log *D* vs *T* inflection point (see later discussion).

Data Analysis. Diffusion out of a plane sheet (infinite film) into an infinite reservoir (e.g., the concentration of the probe outside the slab is close to zero at all time) with a time-independent diffusion constant *D* yields the following solutions[11]

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2}\left[\int_{n=0} \frac{1}{(2n+1)^2}\exp\left\{\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right\}\right] \qquad (1a)$$

$$= 2\left(\frac{Dt}{l^2}\right)^{1/2}\left[\pi^{-1/2} + 2\int_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\left\{\frac{\mathrm{n}l}{(Dt)^{1/2}}\right\}\right] \qquad (1b)$$

where $M(t)$ is the amount of material that has diffused out of the slab at time t. When the left-hand side of eq 1 is less than 0.6, the series in eq 1b can be ignored and

$$\frac{\mathrm{M(t)}}{\mathrm{M}(\infty)} \approx 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} = k_1 \mathrm{t}^{1/2} \qquad (2)$$

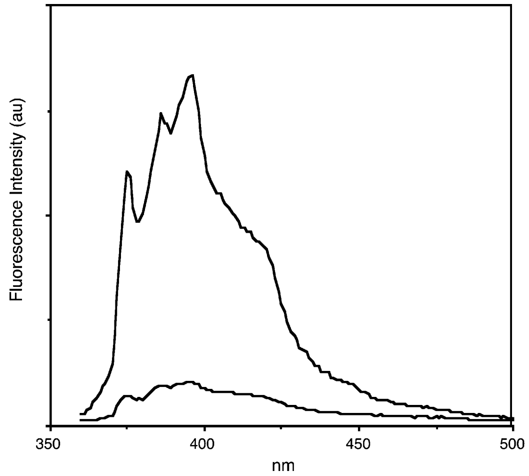

Figure 1. Emission spectra of pyrene in polystyrene film before and after equilibration with CO_2 at 40 °C and 51.8 bar (lower intensity spectra taken after releasing CO_2 from the cell).

When the left-hand side of eq 1a is greater than 0.6 (i.e., at long time), then all the terms for $n > 0$ in the summation in eq 1a can be ignored, from which we obtain

$$\ln\left(1 - \frac{\mathrm{M}(t)}{\mathrm{M}(\infty)}\right) \approx \ln(8/\pi^2) - \frac{\pi^2 Dt}{4l^2} = A + k_2 t \qquad (3)$$

From the slopes k_1 and k_2 we can obtain D. At very low optical density (such as we have in our very thin polymer films) and in the absence of self-quenching (as evidenced by the absence of the pyrene excimer fluorescence) the total fluorescence is proportional to the amount of fluorophore and we may write

$$\frac{M(t)}{M(\infty)} = \frac{I_0 - I(t)}{I_0 - \mathrm{I}(\infty)} = F(t) \qquad (4)$$

I_0 and I_∞ are the initial and limiting fluorescence intensities, respectively.

In principle I_∞ should be related to the distribution of the probe between the film and the CO_2 phase, i.e.

$$\frac{m(\mathrm{CO_2})}{m(\mathrm{PS})} = \frac{[\mathrm{P(CO_2)}]}{[\mathrm{P(PS)}]}\frac{V(\mathrm{CO_2})}{V(\mathrm{PS})} \qquad (5)$$

where m(x) is the total amount of the probe (P) in phase x, [P(x)] is the concentration of the probe and V(x) is the total volume of the phase. The ratio of concentrations is the partition coefficient for the probe and could easily be expected to exceed 10^6 for the PS film compared to the CO_2 phase.[12] However the volume ratio of the polymer film (ca. 3.2×10^{-5} cm^3) to the cell volume (ca. 30 cm^3) is on the order of 10^{-6}, so it is not expected that all pyrene will be removed from the PS film.

Results

Fluorescence Spectra. The emission spectrum of pyrene from doped polystyrene thin film at 40 °C is shown in Figure 1. No obvious excimer fluorescence was found. Following the release of CO_2 from the system at the end of an experiment we find that the shape of the emission spectrum does not change, only its intensity has diminished. The pyrene fluorescence spectrum in contact with CO_2(sc) is essentially identical to Figure 1 but the absolute intensity is changed because of the change of the refractive index in the cell interior (e.g. the optical coupling changes). The rate of decrease in the normalized fluorescence intensity ($I(t)/I_0$) depends strongly on the CO_2 pressure (see Figure 2). As expected, when the pressure is higher, the decay of the intensity is faster. We use the dynamic time base scans to analyze the diffusivity of pyrene in polystyrene film in the presence of carbon dioxide, as described next.

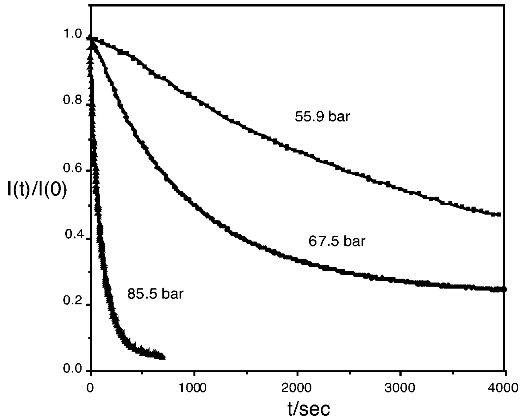

Figure 2. Time-dependent front face emission intensity of pyrene from polystyrene films (ca. 250 nm thickness) at 40 °C under 55.9, 67.5, and 85.5 bar of CO_2.

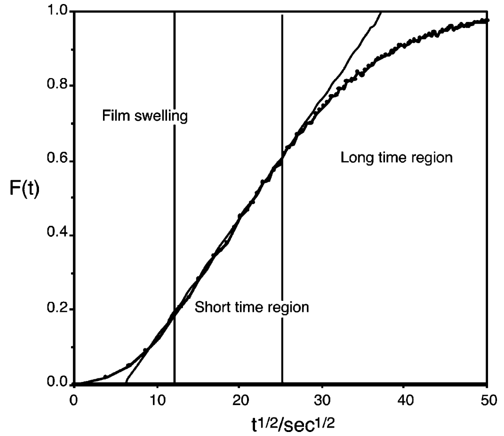

Figure 3. Typical plot of $F(t)$ vs $t^{1/2}$ for pyrene release from polystyrene film (243 nm in thickness) at $P_{CO_2} = 62.3$ bar, T = 60 °C.

Estimation of Diffusion Constants (Pyrene Extraction into CO_2). Upon introduction of the CO_2, the pyrene fluorescence signal begins to drop (there are some optical artifacts at very short time that cause a variation in the fluorescence intensity because of the change of the refractive index on the inside of the cell). In our usual method of analysis we plot the function $F(t)$ as a function of $t^{1/2}$ (see eq 2). As mentioned earlier, the measured fluorescence intensity fluctuates strongly upon the introduction of the compressed CO_2 because of the change of the refractive index inside the cell. Therefore, I_0 is obtained from the intensity extrapolated quadratically to time zero using the first 4−6 points after the introduction of CO_2. I_∞ was directly estimated from the experimental data: when the fluorescence intensity became constant, the average intensity over at least 20 points was taken as I_∞. An example of this kind of plot is given in Figure 3. According to diffusion theory the function $F(t)$ should be linear in $t^{1/2}$ for $0 < F(t) < 0.6$. However at early time there is a clear nonlinearity which must be attributed to time required for the PS film to absorb CO_2 and to reach equilibrium. The linearity is good in the region $0.2 < F(t) < 0.6$ for most of our dynamic data (see Figure 4). In the later stages where $F(t) > 0.6$ we can obtain another good linear relationship in the plot of $\ln(1 - F(t))$ vs t (see Figure 5).

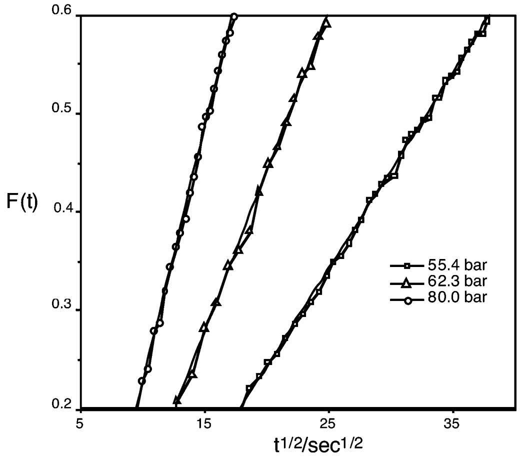

Figure 4. $F(t)$ vs $t^{1/2}$ for polystyrene films with approximately the same thickness (ca. 250 nm) in SCF CO_2 at 80.0, 62.3, and 55.4 bar in the linear region ($0.2 < F(t) < 0.6$).

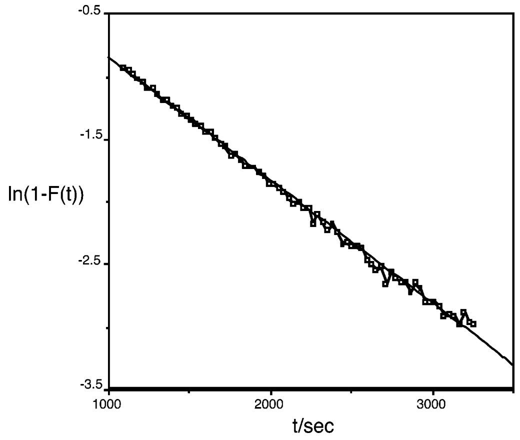

Figure 5. Typical plot of $\ln(1 - F(t))$ vs t for pyrene release from polystyrene film to SC CO_2 at later times ($F(t) > 0.6$) at $P_{CO_2} = 62.3$ bar and 60 °C.

Evidently the solubility of pyrene in the CO_2 phase is rather small, as we have never been able to detect pyrene fluorescence in the right angle optical configuration, which collects fluorescence signal from the bulk CO_2. This suggests that the average concentration of pyrene in the CO_2(sc) phase is less than 10^{-8} M (we can easily detect pyrene fluorescence from a saturated water solution with our fluorimeter[13]). We have found that the pyrene tends to be deposited onto the metallic surfaces of the fluorescence cell. Therefore, the loss of pyrene really consists of the transport of pyrene from the polystyrene film to the metallic surfaces. The details of the loss of pyrene do not matter, so long as pyrene concentration in the exterior solvent does not become significant compared to the concentration in the polystyrene film. Obviously the solubility of pyrene in CO_2(sc) must be sufficiently high that transport from the film is not solubility limited and this factor must be considered in choosing fluorescent probes using our technique.

The values of the diffusion constant were obtained using eqs 2 and 3 (the derived values are denoted D_1 and D_2 respectively) (the experimental values are presented in the Supporting Information for this paper). Note that in the analysis we use the measured thickness of the unswollen film. It is reasonable to assume that all swelling occurs in the dimension perpendicular to the sapphire window because the film is held firmly in place by the sealing gasket. Because the rate of exit scales as the thickness of the film squared, the corrected diffusion constant would be given by $D_{corr} = f^2 D_{meas}$, where f is the swelling coefficient, $V(CO_2) = fV_0$, and D_{meas} is the value we report based on the dry film thickness. This correction will tend to increase the value of the diffusion constant by a factor of ca. 1.1 to 1.2.

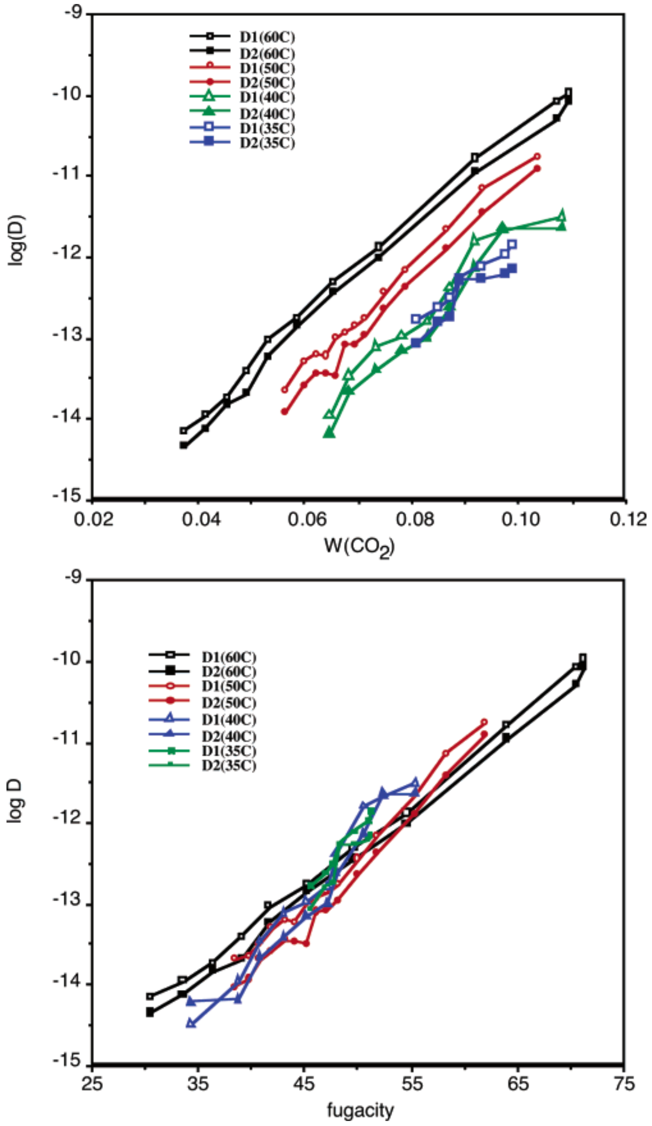

Figure 6. $\log(D)$ vs w_{CO_2} and fugacity for the temperatures indicated, using D_1 and D_2.

We estimated the weight fraction of CO_2 in PS using the data of Wissinger and Paulaitis[14] and the fugacity using the equation of state for CO_2.[15] In Figure 6, we plot the values of $\log(D_1)$ and $\log(D_2)$ as a function of the CO_2 weight fraction in the film and the CO_2 activity for 35, 40, 50, and 60 °C. Our range of w_{CO_2} is approximately the same as Gupta et al.,[5] but the dynamic range of our diffusion constants is quite a bit larger (compare 10^{-14}–10^{-10} cm^2/s with approximately 10^{-13}–10^{-12} cm^2/s). On the other hand Chapman et al.[6] have a larger dynamic range than we do (ca. 10^{-15}–10^{-9} cm^2/s) and go to a lower CO_2 weight fraction (0.02).

Estimation of Diffusion Constants (Pyrene Vaporization). Pyrene sublimes from the PS film into a vacuum in a physical process that is analogous to extraction by CO_2 and the loss of pyrene fluorescence can be treated using the same equations as discussed

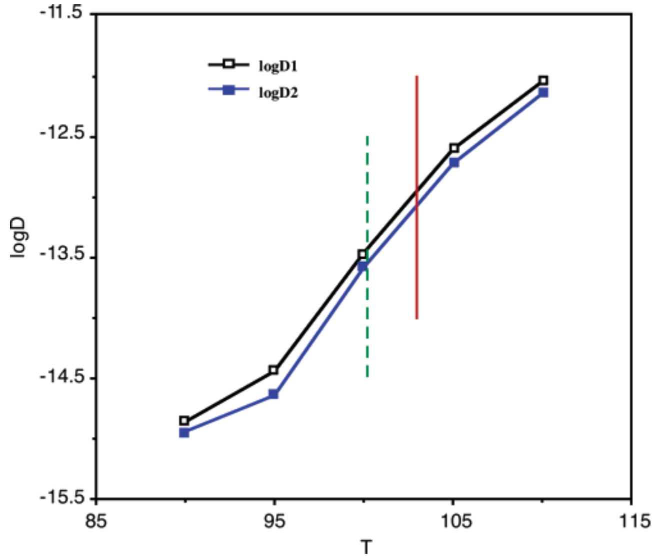

Figure 7. log(D) vs T for release of pyrene into a vacuum. The vertical lines correspond to T_g derived from the inflection point method (dashed line) and DSC measurement (solid line).

Table 1. P_g Values

T (°C)	$P_g^{(1)}$ (bar)^a ($w_g^{(1)}$)	log$D(P_g^{(1)})^b$	$w_g^{(2)c}$
40	49.9 (0.0662)	−13.74	0.0677−0.0709
50	50.4 (0.0586)	−13.45	0.0571−0.0611
60	46.5 (0.0495)	−13.30	0.0474−0.0506

[a] Estimated from the inflection point of the log(D_1) vs P_{CO_2} plot (see text). [b] Estimated value at $P_g^{(1)}$. [c] Estimated using eq 6 from the point at which log(D_1) and log(D_2), respectively, are equal to −13.5.

above to obtain D_1 and D_2. These are plotted as a function of T in Figure 7, and as can be seen, the rate of change of these quantities is relatively large in the region of T_g. We empirically estimated our "T_g" values as follows: The log(D) vs T plot was fit to a cubic equation and the inflection point was found by setting the second derivative equal to zero. While obviously one should not make too much out of the precision of this method, we obtained a value of 100.3 and 100.4 °C from the D_1 and D_2 curves, respectively (log D at this temperature is ca. −13.45). We measured T_g of our polystyrene sample using the inflection point analysis of DSC curves (extrapolating to zero heating rate) and obtain a value of 103 °C (log $D(T_g)$ is ca. −12.93). It is not surprising that different techniques yield slightly different T_g values.

Estimation of P_g Values. The change in the diffusion constant with w_{CO_2} is rather steady for the various temperatures studied (see Figure 6), with a much more dramatic break in the curve for the two lower temperatures (35 and 40 °C). While we emphasize that the method applied to obtain T_g for release of pyrene into a vacuum was empirical (although analogous to standard DSC analysis), we apply a similar approach here. We fit the log(D_1) vs P_{CO_2} to a cubic equation around the region where the diffusion constant is approximately equal to $D(T_g)$ and obtain the inflection point as our estimate of P_g (see Table 1). We prefer to use P_{CO_2} for this calculation because it is measured directly, unlike w_{CO_2} which is derived from empirical relationships. There is so little nonlinearity in log(D_1) vs P_{CO_2} for 50 and 60 °C that we do not believe our P_g values obtained in this procedure can be too accurate.

We have also considered obtaining a T_g value based on the "apparent viscosity" (or friction factor) of the medium. According to the Stokes−Einstein model the diffusion constant is proportional to the ratio of the temperature and the viscosity at a given temperature (assuming a constant molecular volume). If we propose that in the glassy state the effective viscosity acting on the molecule is a constant (with or without the presence of a swelling solvent), then we can write

$$D(T,w_g) = (T/T_g)D(T_g) \qquad (6)$$

where $D(T,w_g)$ denotes the diffusion constant of the probe in a swollen film at the CO_2 content that plasticizes it at temperature T and $D(T_g)$ is the diffusion constant of the unswollen film at T_g. We take the value of log $D(T_g)$ as ca. −13.45, as determined by our vacuum experiment. If we find the value of w_{CO_2} such that eq 6 holds (see Figure 6) then we can estimate the value of w_g and these values are also presented in Table 1. Note that the ratio of temperatures in eq 6 makes very little impact on this estimate as the log of the temperature ratio is in the range −0.05 to −0.08, i.e., below the uncertainty in the values of log D. The values we obtain in this approach are in fair agreement with Figure 3 of ref 6. Obviously if we take as our value of $D(T_g)$ as ca. −12.93, the estimated value of w_g will be substantially higher.

Discussion

On the basis of the data of Chapman et al. [6] for our experimental w_{CO_2} range at 50 and 60 °C PS is entirely in the rubbery state, while for 35 and 40 °C we pass through the rubber−glass transition ($w_{CO_2}{}^g(T)$). For 35 and 40 °C the change in D that we observe near $w_{CO_2}{}^g(T)$ is relatively minor compared to that of Chapman et al.[6] As these authors point out, their azobenzene probe has significantly different polarities in the cis and trans forms, and part of the rapid increase in D below $w_{CO_2}{}^g(T)$ that they observe may be related to the interaction of these probes with the PS matrix. Our pyrene probe has neither a significant dipole or quadrupole moment and is not expected to have any specific interaction with the PS matrix. In any case the "anomalous" increase in D we observe as we pass above $w_{CO_2}{}^g(T)$ amounts to about 1 order of magnitude. This is similar to what we observe from the release of pyrene into a vacuum. All the data of Gupta et al. [5] were collected for a fully plasticized film.

The other general observation is that the overall slope of the log(D) vs w_{CO_2} or fugacity curves are reasonably similar to each other. This observation is similar to the findings of Gupta et al. (see Figure 7 of ref 5) and is what would be expected from the Vrentas−Duda equation.[16] This equation can be written (eq 4, ref 5)

$$\ln(D_{\text{probe}}/D_0) = -\gamma V_{\text{probe}} M_{\text{probe}}/V_{\text{FH}} [(V^*_{CO_2}/V_{CO_2} M_{CO_2} - V^*_{\text{polym}}/V_{\text{polym}} M_{\text{polym}}) w_{CO_2} + V^*_{\text{polym}}/V_{\text{polym}} M_{\text{polym}}] = A w_{CO_2} + \text{constant} \qquad (7)$$

where V^*_i is the critical hole free volume for the ith component and V_i and M_i are the volumes and molecular weight of the ith component. γ is the overlap factor and V_{FH} is the average free volume of the mixture. A in eq 7 is approximately 55, which is fairly similar to the dependence observed by Gupta et al. [5] Of course the exact value should depend on the molar volume of the probe, but in general, one can expect a very large increase in the diffusion constant of any probe as the weight fraction of CO_2 increases, even below the point of plasticization for a given temperature.

These experiments demonstrate the efficiency of CO_2 in increasing the rate at which materials can be added or removed from polymer films, even if the material has a relatively small solubility in CO_2 itself. The present method is simple to apply and because of the sensitivity of fluorescence can be applied to ultrathin films. The obvious disadvantage of this approach is that the probe molecule must be fluorescent, be molecularly dissolved in the film and have sufficient solubility in CO_2(sc) to be transported away from the film. For very small values of the diffusion constant, we would have to use films thinner than the ca. 250 nm used and one would have to be concerned about confinement effects on the plasticization process itself. For diffusion constants larger than about 5×10^{-11} cm^2/s one has to use thicker films or the transport of the probe will be almost finished while the film is still equilibrating with the CO_2 fluid.

If one is willing to accept the proposition that at the glass transition the friction factor (or effective viscosity) is a constant, then by using eq 6 one may estimate the content of CO_2 required to plasticize a film by comparing the loss of probe by diffusion into a vacuum (at T_g) with the loss of the probe into the supercritical fluid at a given temperature. As a practical matter this would require relatively few diffusive loss experiments, which are time-consuming.

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Supporting Information Available: Table S1, containing a compilation of CO_2 pressure, weight fraction of CO_2, fugacity and activity, dry film thickness (l), half-time ($t_{1/2}$), k_1 and k_2, and the corresponding diffusion constants (D_1 and D_2). This material is available free of charge via the Internet at http://pubs.acs.org.

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