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Effect of CO_2 Plasticization on Azobenzene Diffusion in Glassy Polystyrene near the Glass Transition

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Introduction

Compressed gases and supercritical fluids are effective plasticizers and mass transfer agents in a number of novel polymer processing applications. In previous work,[1] we examined how plasticization with CO_2 influences the rate of solute diffusion in glassy polystyrene (PS) near the glass transition. Specifically, we reported the direct measurement of self-diffusion coefficients of the cis and trans isomers of azobenzene (AZ) in PS as a function of CO_2 pressure at 35 °C using forced Rayleigh scattering (FRS). The range of pressures and CO_2 solubilities studied were high enough to lower the glass transition temperature (T_g) to less than 35 °C, thereby allowing AZ diffusivities to be measured across the CO_2-induced glass transition. Our results showed that the diffusion of this FRS dye in CO_2-plasticized PS is enhanced by 2−3 orders of magnitude over values predicted on the basis of T_g depression alone.[2] In contrast, the effect of plasticization by temperature, chain ends, or added diluent is largely accounted for by ($T - T_g$) scaling for dye diffusion in pure PS and in PS plasticized by tricresyl phosphate. In this note, we report FRS measurements of AZ diffusion in PS across the CO_2-induced glass transition for two additional temperatures. These new results are used to compare the effects of plasticization by temperature and by added CO_2 on solute diffusion near the glass transition of PS.

Experimental Section

In FRS, the diffusivity of a photoactive dye is measured by monitoring the relaxation of a "forced" gradient in the dye concentration. At sufficiently low concentrations, this measurement yields a tracer or self-diffusion coefficient. The range of accessible diffusion coefficients ($\sim 10^{-5}-10^{-16}$ cm^2/s) covers much of the range of diffusivities encountered in polymer solutions, melts, and glasses, making the technique well suited to study diffusion across the glass transition.[3]

The experiment involves a writing process to create the dye concentration gradient and a reading process to monitor the time evolution of that concentration gradient. During the writing process a sinusoidal light intensity interference pattern is temporarily established in the sample by crossing two mutually coherent laser beams. Dye molecules in the illuminated region undergo a photoisomerization to produce the photoactive isomer from the thermodynamically stable isomer. Since the extent of the photoisomerization depends on the intensity of the excitation light, two sinusoidal concentration profiles (gratings) are created, one for each isomer. These gratings are 180° out of phase, mimic the periodicity of the light intensity interference pattern, and relax at independent rates as the isomers diffuse due to thermal motion. For Fickian diffusion, each concentration grating remains sinusoidal, while its amplitude decays exponentially in time. Thermal reconversion to the stable isomer also contributes to the relaxation process.

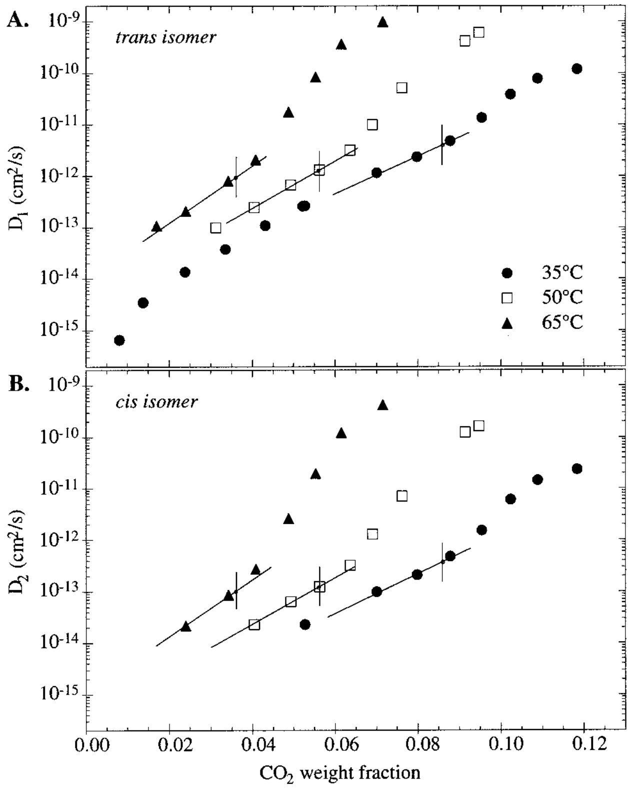

Figure 1. Concentration dependence of the tracer-diffusion coefficient for azobenzene in PS-213K/CO_2. (A) D_1: trans isomer. (B) D_2: cis isomer. Vertical lines denote the CO_2 weight fraction at the glass transition for each temperature, determined by creep compliance.[6] Lines through the data are meant to guide the eye.

The dye concentration profiles produce corresponding profiles in the optical properties of the sample or an optical diffraction grating. The amplitude of that grating can be monitored using a nonexciting (reading) laser, directed at the Bragg angle. In general, both dye concentration gratings contribute to the optical grating. The two isomer diffusivities are often similar, but they are rarely identical due to differences in the molecular size and shape of the isomers, as well as differences in their interactions with the local environment. The result is a nonexponential time dependence for relaxation and, under certain conditions, nonmonotonic decay of the diffracted signal intensity. A detailed description of the FRS technique, our high-pressure apparatus, and the data analysis approach we adopted is given in previous work.[1,4]

Results and Discussion

The measured isomer diffusion coefficients are plotted in Figure 1 as a function of CO_2 weight fraction for the three temperatures studied. The conversion from CO_2 pressure to CO_2 dissolved in the polymer was carried

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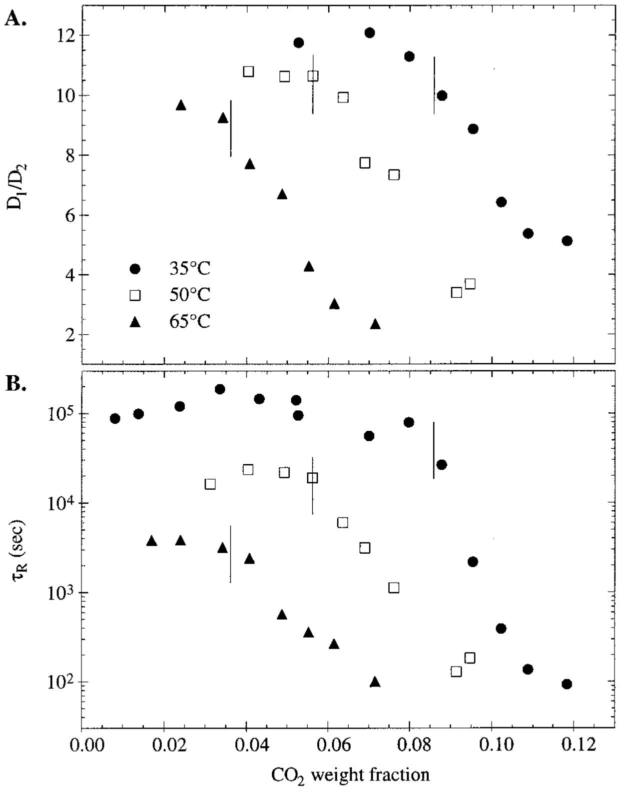

Figure 2. Concentration dependence of the ratio of trans (D_1) to cis (D_2) isomer diffusion coefficients and the cis → trans thermal reconversion time for azobenzene in PS-213K/CO_2. Vertical lines denote the CO_2 weight fraction at the glass transition for each temperature.[6]

out using the Sanchez–Lacombe equation-of-state fit to the measured sorption isotherm at each temperature.[5] The CO_2 weight fraction needed to induce a glass transition at each temperature was likewise calculated from the corresponding sorption isotherm and the measured CO_2 pressure at the CO_2-induced glass transition determined from creep compliance measurements.[6] The ratio of isomer diffusion coefficients and the characteristic time for cis → trans thermal reconversion, τ_R, are plotted as a function of CO_2 weight fraction in Figure 2.

Several observations are made from these results: First, probe mobility at the glass transition is clearly sensitive to the CO_2 concentration. Figure 1 shows that the isomer diffusivities at the CO_2-induced glass transition systematically increase with CO_2 concentration even as the temperature decreases by 30 °C. Since lower dye mobilities are expected with decreasing temperature due to decreased thermal motion, this increase in isomer diffusivities must be governed by the higher CO_2 solubilities in PS at lower temperatures. Second, the effect of the CO_2-induced glass transition on the concentration dependence of probe diffusivity is a distinct increase in slope near the glass transition. Both observations are consistent with previous FRS studies.[2,7]

In contrast, the behavior depicted in Figure 2 is somewhat surprising. The diffusive selectivity (D_1/D_2) and τ_R are both essentially constant below the glass transition but drop dramatically with increasing CO_2 concentration in the melt. Moreover, the magnitude of D_1/D_2 is always substantially greater than 1. These results are unexpected considering (1) the small differences in isomer size and shape, which are invariant across the glass transition, and (2) the fact that AZ isomerization in pure PS is only slightly hindered in the glass relative to the melt.[8,9]

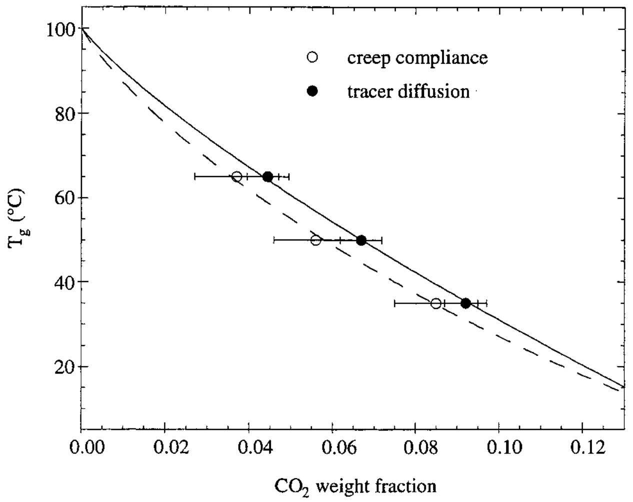

Figure 3. Comparison of CO_2-induced T_g depression in PS/CO_2 as a function of CO_2 weight fraction, determined by macroscopic relaxation and probe diffusion. The lines are fits to the Chow model.[4]

The difference in isomer diffusivities is most likely related to the difference in isomer-PS/CO_2 matrix interactions, attributed to stronger attractive intermolecular interactions between quadrupolar CO_2 and the highly polar cis isomer of AZ, compared to interactions between CO_2 and the nonpolar trans isomer. Such preferential cis AZ–CO_2 interactions would act to reduce cis isomer mobility by increasing the overall coupling of its Brownian motion to the PS/CO_2 matrix. This effect amounts to a higher degree of isomer–matrix cooperativity required for cis isomer translation and should be a strong function of whether the matrix is above or below the glass transition. Increasing the degree of plasticization in the melt, by either increasing temperature or increasing CO_2 concentration, reduces the difference in local environments for the two isomers and drives $D_1/D_2 \rightarrow 1$. A similar argument can be made for the decrease in τ_R with increasing CO_2 concentration: strong coupling to the matrix reduces the mobility of the cis isomer and increases the average reconversion time, so that plasticizing the matrix with CO_2 enhances the rate of isomerization. Increasing the temperature also facilitates isomerization, as expected.

An explanation for why the CO_2-induced glass transition has such a large effect on these parameters is not obvious. We note that both D_1/D_2 and τ_R are local parameters, influenced by matrix dynamics only on the length scale of the isomers. However, a broad distribution of isomer mobilities on this length scale is likely, due to spatial heterogeneity in the local dynamics near the glass transition.[10] The measured values for D_1/D_2 and τ_R are averages over this distribution.[11] The results reported in Figure 2 may reflect, therefore, an additional effect of CO_2 plasticization in the melt, which is to reduce spatial heterogeneity in the local matrix dynamics with increasing CO_2 plasticization at a given temperature. Interestingly, CO_2 does not appear to have the same effect in the glass. A resolution of this issue would benefit from similar experiments with probes of different sizes and polarities.

Finally, close inspection of Figure 1 reveals that the values of the CO_2 weight fraction at the glass transition obtained from the creep compliance measurements[6] are systematically less than those one would estimate from the isomer self-diffusion coefficients. These estimates are obtained from the intersection of linear fits of the isomer self-diffusion coefficients in the glass and in the melt. The CO_2 weight fraction at the glass transition derived from the creep compliance and self-diffusion coefficient measurements at 35, 50, and 65 °C are plotted as a function of CO_2 weight fraction in Figure 3. The values determined from the creep compliance measurements were estimated using a convention that locates the glass transition at the intersection of linear fits of compliance vs CO_2 pressure in the glassy and transition regions. Using instead the inflection point of the compliance vs CO_2 pressure curve in the transition region (i.e., the midpoint convention) gives systematically higher values for the amount of CO_2 required to induce a glass transition.[12] The effect is to shift the CO_2 weight fractions from the creep compliance measurements by roughly +0.01 for all three temperatures, which brings these results into good agreement with the CO_2 concentrations obtained from the self-diffusion measurements.

References and Notes

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